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(54) PROCESS FOR CONTINUOUS PREPARATION OF WATER-SOLUBLE POLYMERS

(71) We, CASSELLA FARBWERKE MAINKUR AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 6 Frankfurt (Main)-Fechenheim, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

Water - soluble homopolymers and / or copolymers, in particular those based on acrylamide, have a continuously growing importance, for instance, as textile finishing agents, binding agents and thickening agents, and especially as floculating and sedimentation auxiliaries.

Highly water-soluble homo and copolymers of acrylamide having a high molecular weights may be obtained, for example, by use of a redox catalyst system containing as reducing component a compound of the general formula

$$R—SO_2—\underset{\displaystyle R''}{\underset{|}{CH}}—NH—COOR'$$

wherein R, R′, and R″ represent alkyl, cycloalkyl, aryl, nitroaryl, halogenoaryl or aralkyl radicals, and R″ may also represent hydrogen (see Belgian Patent No. 701,722).

At room temperature, polyacrylamide solutions formed when carrying out the polymerization in an aqueous medium have a sticky, gelatinous or gummy consistency and, consequently, are difficult to process, for instance to stir or to remove from the reaction vessels.

Precipitation polymerization in organic solvents, which would appear to be a solution of these difficulties, only yields polymers having a relatively low molecular weight.

Known polymerization plants having in the interior revolving cylinders which rotate relatively to each other (DAS 1 301 068) or plants having other rotating devices (DAS 1 301 522) or a longish rotor of an oval cross section (DAS 1 301 523) or polymerization plants such as planet extruders in the form of rollers (DOS 1 595 735) have not proved useful for the preparation of water-soluble polymers by polymerization in water. Moreover, such apparatus are complicated. Many attempts have been made to prepare water-soluble polymers in a reaction tower by continuous polymerization in an aqueous medium. It is known (DAS 1 218 157, col. 1, lines 28—41) that these efforts have failed because, after only a short time, the slightly viscous monomer solution which is introduced at the upper end of the reactor cleared a way through the highly viscous polymer solution and came out of the reactor at the bottom in an unpolymerized or only slightly polymerized state. Even the installation of obstacles such as sewage blocks or Raschig rings did not prevent the formation of such channels.

Consequently, it has been necessary to adopt batchwise preparation for water-soluble polymers, in particular those based on acrylamide, by polymerization in an aqueous medium.

By employing a cylindrical reactor equipped with shutoff joints and a piston which is movable along the cylinder axis it is possible to carry out the batchwise polymerization (DAS 1 218 157). The piston is moved either with the aid of air or water pressure, or mechanically.

According to the known processes for polymerization in an aqueous solution the polymers are obtained in the form of jellies which may, of course, be reduced according to the known methods to small particles, but almost immediately fuse together. Consequently, the dehydration of the gelatinous polymers is not immediately possible and requires, for instance,

the introduction of the gelatinous polymer particles into a water-immiscible organic liquid which is incapable of dissolving the polymer and, furthermore, requires the elimination of the water by way of an azeotropic distillation (DAS 1 494 967).

It is an object of the present invention to provide a simple process for the production of water-soluble polymers by polymerization in an aqueous medium, which avoids the disadvantages of the hitherto known processes, in that it may be carried out continuously and yields particularly high-molecular weight products.

According to the invention, there is provided a process for continuous preparation of a water-soluble polymer comprising the steps of continuously introducing, at the top of a vertical, elongated reactor, an aqueous solution or dispersion of a monomer which forms a water-soluble polymer, a catalytic amount of a redox catalyst system including a reducing agent of the formula:

$$R\text{—}SO_2\text{—}\underset{\displaystyle R''}{\underset{|}{CH}}\text{—}NH\text{—}COOR'$$

wherein R, R′ and R″ represent alkyl, cycloalkyl, aryl, nitroaryl, halogenoaryl or aralkyl radicals and R″ may also represent hydrogen, maintaining the solution or dispersion at a pH above 7, adjusting the throughput of said aqueous solution or dispersion and its temperature to form a stationary polymerization zone in said reactor in which a gel of polymer having a high molecular weight is formed, and continuously discharging said gel at the base of said reactor.

Preferably the monomer comprises 15 to 40% by weight of the aqueous solution or dispersion.

Preferably the process is carried out in a reactor, the internal wall of which consists of a material having a contact angle to water of over 45°, whereby the polymer is prevented from sticking to said internal wall.

Preferably also the stationary polymerization zone is formed in the upper third of the reactor and is preferably 15—40 cm high.

The gelatinous polymer solution formed in the course of the process may be mechanically reduced to small particles which are subsequently dehydrated. These particles do not tend to fuse together and, consequently, may be dried in a conventional manner, for instance, on a belt-type dryer.

It is possible by the method of the invention to polymerize continuously all monomers capable of forming water-soluble polymers, e.g. acrylamide, acrylic or methacrylic acid, N-vinylmethylacetamide or vinylsulfonic acid. Apart from those monomers, other vinylmonomers forming themselves water-insoluble polymers may be present in such amount as secures the water-solubility of the mixed polymer being formed. Thus, it is possible that, based on the monomer yielding water-soluble polymers, up to 30% by weight of, for instance, methacrylamide, a vinyl ester, an acrylic or methacrylic ester or acrylonitrile may be present in the aqueous monomer solution or dispersion employed.

In order to start the polymerization, the components of the redox catalyst system are added to the monomer solution or dispersion in the polymerization reactor preferably after having been mixed with each other.

Suitable reducing components in the redox catalyst system are for instance: ethyl N-p-tolylsulfone methyl carbamate, methyl N-p-nitrophenylsulfone methyl carbamate, methyl N-p-chlorophenylsulfone methyl carbamate.

Suitable oxidizing components are for instance: benzoylperoxide, ammonium or potassium peroxide disulfate, methylethylketone peroxide, hydrogen peroxide, cumolhydroperoxide, atmospheric oxygen and other organic or inorganic per-compounds. Suitable co-catalysts are dibutylamine hydrochloride, copper acetylacetonate and copper sulfate. The use of additional co-catalysts is advantageous but not absolutely necessary.

The monomer solution containing the redox catalyst system and being introduced into the polymerization reactor, is adjusted to a pH-value above 7, normally between 7 and 10. A pH-value above 7 is necessary for the formation, under the reaction conditions of the process, of polymers which are definitely not cross-linked at all and, consequently, are completely water-soluble. In most cases it is advisable to adjust the pH-value to 7,5—8,8. If, under the instant reaction conditions and at a pH-value of 8—10, saponifiable monomers are employed, a saponification sets in which allows the preparation of copolymers from a single monomer.

Among the reaction conditions of the present invention, a decisive factor for a successful continuous polymerization is the use of the specified redox catalyst system which is described in Belgian Patent No. 701,722. Other catalyst systems yield only relatively low-molecular weights, or, if higher concentrations are employed, cross-linked polymer jellies which, for instance due to the formation of channels, do not allow continuous polymerization or only yield incompletely water-soluble polymers.

In general, the redox catalyst system containing aqueous solution or dispersion of the polymerizable monomer or monomer mixture is introduced into the reactor at temperatures ranging from −10 to +20°C. If low percentage solutions or dispersions (i.e. about 15—20% by weight) are employed, temperatures may rise up to 50°C.

The polymerization plant being used according to the present invention is a vertical

reactor which may be without any internal structure, either moving or stationary. For the sake of simplicity a reactor of circular cross section is preferred. It is, however, also possible to use reactors having other cross sections, for instance square, rectangular or elliptical.

The preferred circular cross section reactor consists of a simple vertical tube. In tests so far made, tubes having an inside diameter of 8—45 cm and a height of 0.80—3 m have been found suitable. The ratio of the diameter and the height was from 1:1.7 to 1:25. In a simple tube of a diameter of 20 cm and a height of 3 m, for instance, it is possible to prepare 50 tons per year of polyacrylamide.

The material constituting the interior surface of the reactor should be of such a nature as avoids any adhesion thereto of the gelatinous polymer solution being formed. Experiments indicate that such characteristics are inherent in materials having a contact angle relative to water of more than 45°C.

Examples of such materials are: polyolefines such as polyethylene and polypropylene; halogenated polyolefines such as polytetrafluoroethylene, polytrifluoroethylene, polyvinylchloride; silicon rubber; and glass fibre reinforced epoxy and polyester resins.

Due to the greater adhesion to the polymers being formed, neither metallic materials such as iron, stainless steel, copper or aluminum, nor non metallic materials such as glass or enamel, are well suited for this application.

The reactor may consist entirely of one single material which resists adhesion of the gelatinous polymer solution being formed. Thus it may consist of a polyethylene, polypropylene, polytetrafluoroethylene or polytrifluoroethylene tube, or alternatively a tube of a material such as concrete or metal, provided with an interior surface layer meeting the above requirements. Thus, for instance, the interior surface of a metal tube may be coated with polypropylene or any other appropriate material.

The invention is described further with reference to the accompanying drawings in which:

Figure 1 shows diagrammatically apparatus for carrying out the process of the invention, and

Figure 2 shows a modification of the apparatus of Figure 1.

The apparatus of Figure 1 broadly comprises a reactor (1), a mixer (2), a comminuting device (3) and a conveyor (4).

In the illustrated embodiment the reactor (1) is a vertical tube, open at its upper and lower ends, and formed preferably of polypropylene, polyethylene, polytetrafluoroethylene or polytrifluoroethylene.

A polymerizable solution or dispersion of a monomer or mixed monomers is introduced into the mixer (2) through an inlet conduit (5). The oxidizing and reducing components of the redox catalyst system are separately introduced, preferably as a solution, through inlet conduits (6) and (7). Co-catalysts, if used, such as copper and/or chloridiones may already have been added to the monomer solution or dispersion which is introduced through the inlet conduit (5), the pH-value of which solution has already been adjusted so that the solution or dispersion introduced into the polymerization reactor will have the desired pH-value above 7. If an even more exact adjustment of the pH-value is required it is possible to add dissolved ammonia or alkali in the mixer through a pipe (5a). The monomer solution or dispersion and the components of the catalyst system are mixed with the aid of a stirrer (8). The mixer (2) is equipped with a heating or cooling jacket (9) through which flows a heat exchange agent, this latter being introduced through an inlet conduit (10) and led off through a discharge conduit (11). In general, the mixture is cooled down in the mixer (2) to −10 to +20°C. Subsequently, the mixture is introduced into the polymerization reactor (1) through an inlet conduit (12) whereby the feed rate to the reactor and thus the throughput of the reactor may be controlled by a dosage valve (13). In the polymerization reactor (1), polymerization commences at a slow rate and with a slight increase in temperature and viscosity. Thus, in the upper part of the reactor, the temperature and the viscosity increase from the top to the bottom. The increasing viscosity reduces the mobility of the growing chains of the polymer molecules, whereas the monomer molecules may still migrate quite freely to the reaction site. Normally, a break in the chain occurs if 2 growing chains react with each other. Since, however, the growing chains are reduced in their mobility, the breaking of the chains is slowed down and finally suppressed. Thus, products are obtained having a particularly high molecular weight.

This effect is known as the gel or Trommsdorf effect. Until now, it could not be applied, however, to the continuous preparation of water-soluble polymers. The retardation or the suppression of the breaking of the chains causes an increase in the polymerization rate whilst, due to the gelatinous constitution of the polymer, the heat of polymerization is not readily dissipated. The gelatinous solution which leaves the bottom of the reactor is discharged at such a rate that, due to the interaction of the rate of polymerization and the reducing heat dissipation as polymerization progresses, a stationary polymerization zone (14) is formed in which the temperature suddenly rises relative to that above the zone (14). This zone reaches a height of about 15—40 cm if the throughput rate in the reactor is chosen so that the zone (14) is formed about

one third of the way down the reactor, as has proved advisable in order to achieve an optimum output.

In the polymerization of a 25% by weight acrylamide solution having a starting temperature of approx. 20°C this is normally achieved if the throughput rate of the reactor is about one third of its content every 30—75 minutes. If a lower throughput rate is chosen, the polymerization zone (14) is formed higher up in the reactor, the maximum capacity of the polymerization reactor is not realized, and the height of the polymerization zone decreases. On the other hand, if a higher throughput rate is chosen, the zone (14) is formed further down the reactor and, as a consequence thereof, the temperature of the gelatinous polymer which comes out of the reactor rises and it may be incompletely polymerized. In consideration of the molar polymerization heat and the temperature at which the solution or dispersion is introduced into the polymerization reactor (1) the monomer concentration is adjusted so as to prevent the maximum temperature of the polymerization process, i.e. the temperature in the polymerization zone (14), surpassing the boiling point of the water. Within the polymerization zone (14) a polymerization gel is formed, the polymer of which has, due to the use of a redox catalyst system according to Belgian Patent No. 701,722, such a high molecular weight as to secure, by reason of its consistency, hermetic sealing of the cross-section of the reactor which prevents the unpolymerised monomer solution or dispersion from working down past the polymerization zone. Consequently, the formation of the polymerization zone (14) preferably having a height of 15—40 cm, in which very high-molecular polymers are formed, is a decisive factor in achieving successful continuous polymerization.

Below the polymerization zone (14) little polymerization takes place and the temperature of the polymer decreases. It is advisable to choose, in the case of a given throughput rate, the height of the reactor, or in the case of a given height, the throughput rate so that, at the bottom of the reactor, the polymer comes out at a normal or only slightly increased temperature.

The polymer solution coming out of the reactor (1) is a gel (15) which is guided and continuously pulled down by two revolving discharge cylinders (16a) and (16b). The gel may subsequently be treated as desired. In the case of the plant illustrated in Figure 1 of the drawing, the gel enters a funnel (17) of the comminuting device (3) where it is engaged by the screw (18), transported to the right (as seen in the drawing) and pressed against an extrusion die (19). Before the die rotates a cutter bar (21) which is mounted onto the screw shaft (20). The gel particles (22) which come out of the comminution device (3) fall onto the conveyor (4) which transports them with a view to any further treatment such as drying. Due to the fact that the polymer particles no longer tend to fuse together they are easy to dry for instance with the aid of a current of heated air. If desired, the dried particles may then be subjected, for further size reduction purposes, to an additional grinding process.

It is advisable but not absolutely necessary to carry out the mixing of the reaction ingredients and their introduction into the polymerization reactor in the presence of a protective gas such as nitrogen. For this purpose, the protective gas is introduced through an inlet conduit (23) into the upper part of the mixer (2) from which it then escapes through a pipe (24). Through a pipe (25), the protective gas is also blown onto the content of the polymerization reactor (1). The two pipes (24) and (25) may be directly connected.

According to the dimensions, in particular the diameter of the reactor employed, the gelatinous solution may be discharged therefrom in two completely different ways.

The first alternative occurs if polymerization reactors having a diameter of up to 15 cm are used. In this case, the gelatinous polymer solution does not leave the reactor spontaneously, but has to be discharged in an appropriate manner. In the plant illustrated on Figure 1, the cylinders (16a) and (16b) serve as a discharge device. Whilst guiding the gel (15) they continuously pull it out of the bottom of the reactor. Instead of using the discharge cylinders illustrated in Figure 1, it is also possible to use other means for discharging the polymer. One such alternative is shown in Figure 2 and consists in leading through the reactor (1) an endless steel line (30) which runs over the fixed rolls (26), (27), (28) and (29), at least one of which, for example the roll (27), is driven counter-clockwise. The steel line (30) is moved through the reactor at the throughput rate. Consequently, the polymerization occurring in the reactor results in the gel being formed around it, the latter being drawn out of the reactor (1) by the movement of the line. By deviation over the roll (26) the steel line (30) is caused to cut out of the gel which then moves on down. Instead of using a steel line it is also possible to choose a different material or a chain. In the latter case the (26) to (29) are replaced by gears. Figure 2 does not show the mixer and the comminuation device. Where in Figures 1 and 2 the same reference numbers are used, they indicate the same parts. Measuring devices for pH-values and temperatures, mechanical drives, pumps etc. are not illustrated in Figures 1 and 2. In this respect, suitable known devices may be employed. If polymerization reactors having a diameter of at least 20 cm are used, the gelatinous solution

automatically comes out of the reactor due to its own weight. It is possible to prevent in an appropriate manner the gelatinous solution from coming out of the reactor too rapidly. For this purpose the rotation rate of the discharge cylinders is slowed down or the reactor is mounted immediately upon the comminuation device, whereby it is the rate of the mechanical feeding in the comminuation device which controls the throughput rate of the reactor.

With the process of the present invention it is possible to carry out during the polymerization process chemical reactions such as saponifications and methylolations. Thus, it is, for instance, possible to prepare copolymers of acrylamide and acrylic acid merely by adding to the acrylamide solution or dispersion to be introduced into the reactor such an amount of alkali in the form of alkali hydroxides, carbonates or hydrogen carbonates, as is necessary for achieving, under the conditions of the process during the polymerization process, a partial saponification.

The polymers prepared according to the process of the present invention distinguish themselves by a particularly high molecular weight of more than 3 million and are, moreover, completely water-soluble. They are excellently suited as flocculating and sedimentation auxiliaries.

A further outstanding property of the polymers prepared according to the present invention is the inherent shape retention, i.e. their ability to keep their given shape.

The following examples are given for the purpose of illustrating the present invention. The percentages are given in percentages by weight.

EXAMPLE 1

10 kg. of a monomer solution containing 24.73% acrylamide, 74.29% water, 0.86% sodium carbonate, 0.024% methyl N - p - tolylsulfone methyl carbamate, 0.048% di-n-butylamine hydrochloride, 0.024% ammonium peroxide disulfate and 0.24% of a copper acetylacetonate solution (1 kg. solution corresponds to 12,3 γCu^{2+}) are introduced at 20°C. into a vertically mounted polypropylene tube having a length of 150 cm. and an inside diameter of 10 cm. At the beginning the bottom of this tube is closed. After 45 minutes' time the polymerization begins in, the temperature of the reaction mixture rising in the course of 25—30 minutes to a maximum of 93°C. After the decay of the reaction temperature down to 30—40°C. a rubber-like, non-sticky polymerization jelly is formed. The reactor is opened at the bottom and the polymer mass is pulled out to such a degree as allows it to be led between two discharge cylinders mounted immediately below the reactor. Subsequently, at the top, 2 kg of the monomer solution having the above-described constitution are added. After 10 minutes' time about, in the upper third of the reactor the polymerization of the subsequently introduced monomer solution sets in. In this moment the mechanically driven discharge cylinders are set going, thus continuously pulling out the polymer mass whereas, at the top of the reactor the corresponding amount of the above-described monomer solution is simultaneously introduced from a mixing vessel.

According to the present invention, the feed rate of the monomer and the offtake rate of the polymer are adjusted so as to allow the formation, in the upper third of the reactor, of a stationary polymerization zone (14). Thus are obtained, per hour, 4 to 5 kg of a high-molecular non-sticky polymer jelly which is reduced into small particles, these particles which do not fuse together being dehydrated on a belt-type dryer so as to form a granulate which is then ground. The thus obtained powdery polymer is completely water-soluble. The relative viscosity of an aqueous solution containing 1 mol sodium nitrate and 0,05% of the polymer is 1,60 at a temperature of 25°C. The product is excellently suited as floculating and sedimentation auxiliary.

EXAMPLE 2

Analogously to the description given in Example 1, a monomer solution consisting of 24,45% acrylamide, 73,30% water, 2,13% sodium carbonate, 0,024% methyl N-p-tolyl sulfone methyl carbamate, 0,024% ammonium peroxide disulfate, 0,048% di-n-butylamine hydrochloride, 0,024% copper acetylacetonate solution (1 ml solution corresponds to 12,3 γCu^{2+}) are polymerized in a tubular reactor having a length of 2 m and an inside diameter of 20 cm and an internal surface consisting of polyethylene. Because of the given dimensions and because the polymer mass is pressed out of the reactor due to its own weight the discharge cylinders mounted at the bottom part of the reactor have to exert a braking effect. Obtained are, per hour, 38 kg of a polymer jelly which is reduced to small particles, the latter being dried in a current of heated air and ground. The powdery final product gives a clear solution when dissolved in water and has, at a temperature of 25°C. a relative viscosity of 1,58 related to an aqueous solution containing 1 mol sodium nitrate and 0.05% of the polymer. The analysis by titration of the carboxyl groups reveals that by the addition of the sodium carbonate about 5 mol % of the acrylamide units are hydrolized during the polymerization so as to yield the sodium salt of the acrylic acid. The product is excellently suited as floculating and sedimentation auxiliary.

WHAT WE CLAIM IS:—

1. A process for continuous preparation of a water-soluble polymer comprising the steps

of continuously introducing, at the top of a vertical, elongated reactor, an aqueous solution or dispersion of a monomer which forms a water-soluble polymer, a catalytic amount of a redox catalyst system including a reducing agent of the formula:

$$\begin{array}{c} R{-}SO_2{-}\underset{\displaystyle R''}{\underset{|}{CH}}{-}NH{-}COOR' \end{array}$$

wherein R, R′ and R″ represent alkyl, cycloalkyl, aryl, nitroaryl, halogenoaryl or aralkyl radicals and R″ may also represent hydrogen, maintaining the solution or dispersion at a pH above 7 at, adjusting the throughput of said aqueous solution or dispersion and its temperature to form a stationary polymerization zone in said reactor in which a gel of polymer having a high molecular weight is formed, and continuously discharging said gel at the base of said reactor.

2. A process as set forth in claim 1 wherein said monomer comprises 15—40% by weight of said aqueous solution or dispersion.

3. A process as est forth in claim 1 or 2, wherein said monomer is acrylamide.

4. A process as set forth in any of the preceding claims wherein a vinyl monomer forming a water-insoluble polymer comprises such a proportion, up to 30% by weight of the water soluble monomer content said aqueous solution or dispersion, as does not affect the water-solubility of the ultimate mixed polymer obtained from said process.

5. A process as set forth in any of the preceding claims wherein said polymer has a molecular weight of over three million.

6. A process as set forth in any of the preceding claims wherein said catalyst system contains an oxidizing component a percompound or atmospheric oxygen.

7. A process as set forth in claim 6 wherein said oxidizing component is benzylperoxide, ammonium or potassium peroxide disulfate, methylethylethylketone peroxide, hydrogen peroxide or cumolhydroperoxide.

8. A process as set forth in any of the preceding claims wherein said polymerization zone is maintained approximately third of the way down said reactor.

9. A process as set forth in claim 8 wherein the height of said stationary polymerization zone is 15—40 cm.

10. A process as set forth in any of the preceding claims wherein said reducing agent is ethyl N - p - tolylsulfone methyl carbamate, methyl N - p - nitrophenylsulfone methyl carbamate or methyl N - p - chlorophenylsulfone methyl carbamate.

11. A process as set forth in any of the preceding claims wherein said aqueous solution or dispersion also includes a catalytic amount of a co-catalyst and said co-catalyst is dibutylamine hydrochloride, copper acetylacetonate or copper sulfate.

12. A process as set forth in any of the preceding claims wherein said pH value is maintained from 7 to 10.

13. A process as set forth in claim 12 wherein said pH value is maintained from 7.5 to 8.8.

14. A process as set forth in any of the preceding claims wherein said monomer comprises a saponifiable monomer and said pH value is maintained at 8—10 to cause the polymer to be a copolymer of the starting material and the saponified derivative.

15. A process as set forth in any of the preceding claims wherein said aqueous solution or dispersion is introduced into said reactor at a temperature ranging from −10° to +50°C.

16. A process as set forth in claim 15 wherein said aqueous solution or dispersion is introduced into said reactor at a temperature ranging from −10° to +20°C.

17. A process as set forth in any of the preceding claims wherein said reactor is circular in cross-section and has a diameter to height ratio ranging from 1:1.7 to 1:25.

18. A process as set forth in any of the preceding claims wherein the temperature of said aqueous solution or dispersion and concentration of said monomer are adjusted to prevent the temperature in said polymerization zone from exceeding the boiling point of water.

19. A process as set forth in any of the preceding claims wherein said height of said reactor and the throughput rate are arranged to provide discharge of said polymer at temperature no more than slightly above ambient temperature.

20. A process as set forth in any of the preceding claims wherein drag is exerted upon said polymer in the direction of the length of said reactor to control its discharge from said reactor.

21. A process as set forth in any of the preceding claims wherein said aqueous solution or dispersion is enveloped in an inert atmosphere.

22. A process according to any of the preceding claims, carried out in a reactor the internal wall of which consists of a material having a contact angle relative to water of over 45° whereby said polymer is prevented from sticking to said internal wall.

23. A method according to claim 11, wherein said internal wall is made of a polyolefin.

24. A method according to claim 24 wherein said internal wall is made of polyethylene, polypropylene, polytetrafluoroethylene, polytrifluororethylene, polyvinylchloride, silicon rubber, glass fibre-reinforced epoxy or polyester resin.

25. A method according to any of the preceding claims carried out in cylindrical reactor

having an inside diameter of from 8 to 45 cm. and a height of from 0.8 to 3 meters.

26. A method according to any of the preceding claims where the throughput of the reactor is controlled by adjusting the discharge rate of the gel using discharge control means at the base of the reactor.

27. A process for the continuous preparation of a water insoluble polymer, substantially as hereinbefore described with reference to Figure 1 or Figure 2 of the accompanying drawings.

28. Water soluble polymer gels, whenever prepared by a method according to any of the preceding claims.

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1317408 COMPLETE SPECIFICATION

2 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

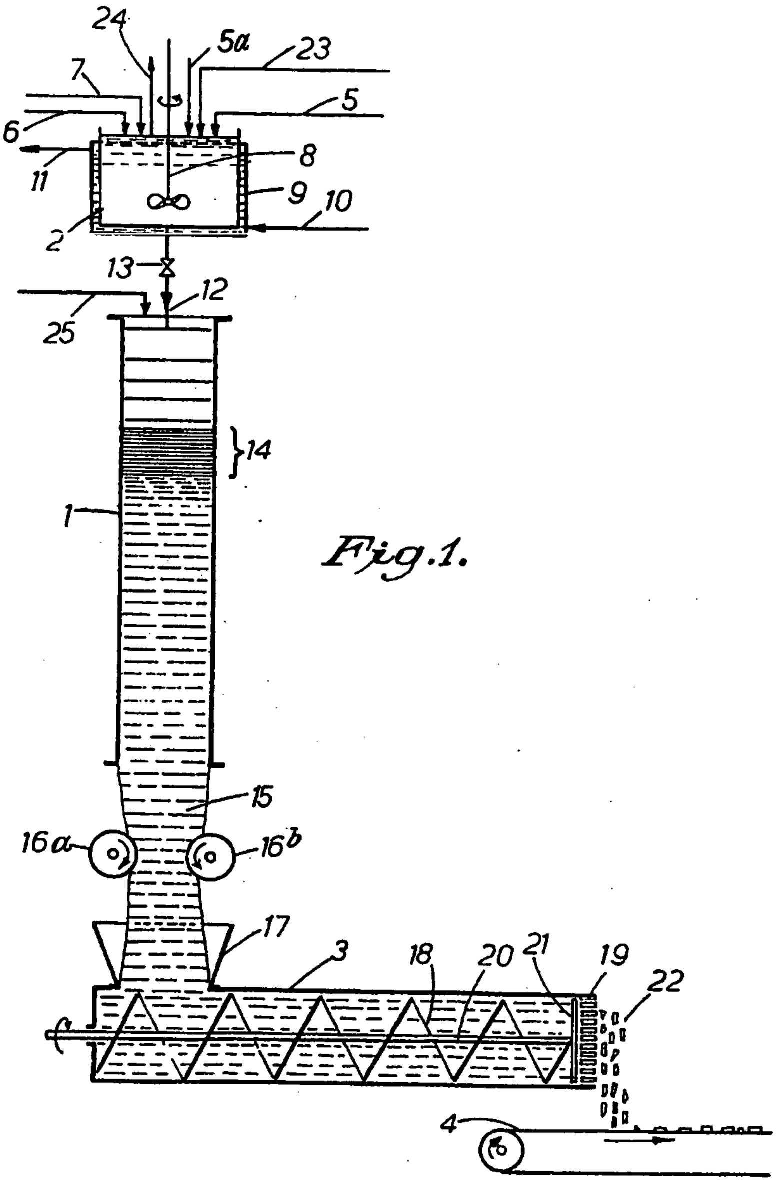

Fig.1.

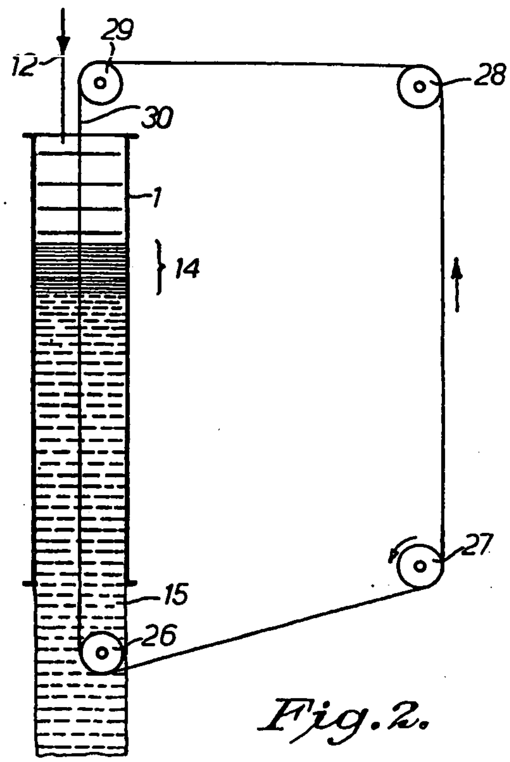

Fig. 2.